

A Multifunctional Coating for Autonomous Corrosion Control

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ABSTRACT

Nearly all metals and their alloys are subject to corrosion that causes them to lose their structural integrity or other critical functionality. Protective coatings are the most commonly used method of corrosion control. However, progressively stricter environmental regulations have resulted in the ban of many commercially available corrosion protective coatings due to the harmful effects of their solvents or corrosion inhibitors. This work concerns the development of a multifunctional smart coating for the autonomous control of corrosion. This coating is being developed to have the inherent ability to detect the chemical changes associated with the onset of corrosion and respond autonomously to indicate it and control it. The multi-functionality of the coating is based on microencapsulation technology specifically designed for corrosion control applications. This design has, in addition to all the advantages of existing microcapsulation designs, the corrosion controlled release function that triggers the delivery of corrosion indicators and inhibitors on demand, only when and where needed. Microencapsulation of self-healing agents for autonomous repair of mechanical damage to the coating is also being pursued. Corrosion indicators, corrosion inhibitors, as well as self-healing agents, have been encapsulated and dispersed into several paint systems to test the corrosion detection, inhibition, and self-healing properties of the coating.

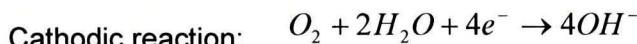
Key words: Corrosion, coating, autonomous corrosion control, corrosion indication, corrosion inhibition, self-healing coating, smart coating, multifunctional coating, microencapsulation.

INTRODUCTION

Nearly all metal and their alloys are subject to corrosion that causes them to lose their structural integrity or other functionality. It is essential to detect corrosion when it occurs, and preferably at its early stage, so that action can be taken to avoid structural damage or loss of function of metals and their alloys. Because corrosion is mostly an electrochemical process, pH and other electrochemical changes are often associated with it, so it is expected that materials that are pH, or otherwise electrochemically responsive, can be used to detect and control corrosion. The authors developed a controlled-release system that consists of pH-triggered release microcapsules that can be incorporated into coatings for early detection of corrosion and for corrosion protection.¹ A multifunctional coating can be formulated by incorporating encapsulated corrosion indicators, corrosion inhibitors, and self-healing systems. The versatility of the microcapsules allows the incorporation of the desired corrosion control functions, singly or combined, into a smart coating. The following sections will describe the relation between pH and corrosion, the design of pH sensitive microcapsules and their synthesis, as well as selected test results obtained by incorporating them into coatings to test their corrosion indication and inhibition functions. Results obtained from the synthesis and evaluation of candidate microcapsule-based self-healing systems, when incorporated into selected corrosion protective coatings, will also be reported.

Corrosion and pH

Corrosion is for the most part an electrochemical phenomenon, because, in most cases, it involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. For instance, when iron corrodes in near neutral environments, the typical electrochemical reactions are:



In the case of localized corrosion, such as pitting corrosion (Figure 1), the anodic reaction occurs in a confined area and the metal ions produced are precipitated as solid corrosion products, such as iron(II) oxide, $Fe(OH)_2$, (often further oxidized to iron(III) oxide, $Fe(OH)_3$), which cover the mouth of the pit. This porous cap covers the solution in the pit and allows the buildup of hydronium ions, H^+ inside the pit. The overall effect is that, while localized corrosion happens, the anode area often has an acidic pH and the cathode has an alkaline pH.²

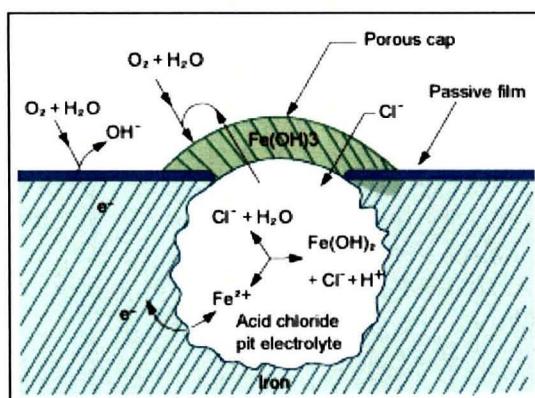


Figure 1: The electrochemical cell set up between anodic and cathodic sites on an iron surface undergoing pitting corrosion.

Besides pitting, crevice corrosion and dissimilar metal corrosion result in pH changes as illustrated by the simple demonstration shown in Figure 2 where a universal pH indicator was used to show the pH changes that occur during corrosion of a metal, such as steel. In this demonstration, most of the steel was exposed to water while a strip in the middle was wrapped in copper tape. The color change of the pH indicator shows that the exposed steel tends to be acidic (yellow color) while the strip wrapped in the copper tape tends to be basic (purple color) due to the oxygen reduction reaction and the release of the hydroxide ion, OH⁻.

Since pH and other electrochemical changes are often associated with corrosion, it is expected that materials that are pH or otherwise electrochemically responsive can be used to detect and control corrosion. Various pH and electrochemically responsive materials as well as their potential applications in smart coatings for corrosion control can be found in our previous review.² Self healing coating is another new development in material design that is important to corrosion control.³⁻⁵

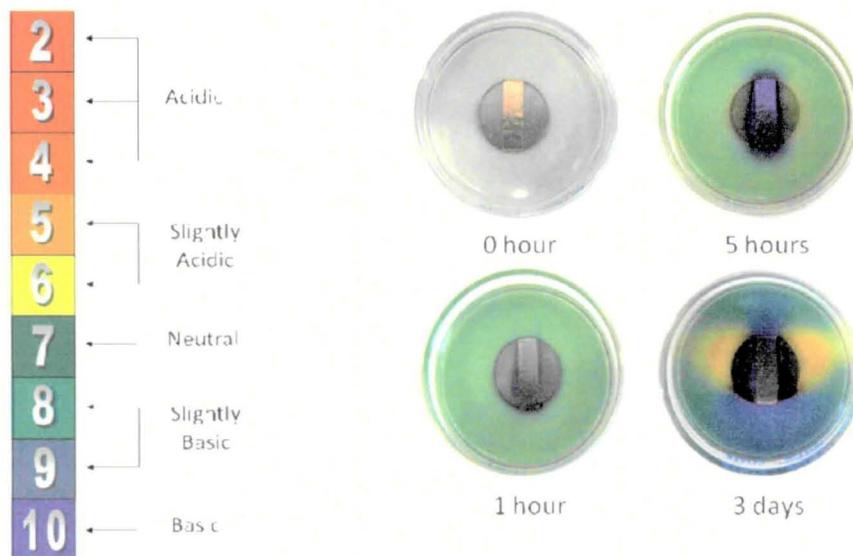


Figure 2: pH Changes associated with corrosion.

pH sensitive Microcapsules

The authors developed pH-triggered release microcapsules for early corrosion detection and corrosion protection.^{1,3,7,8} The pH sensitive microcapsule has a wall designed to break down and release the core contents in response to the pH of the cathodic site of localized corrosion. Figure 3 shows a conceptual illustration of how an encapsulated corrosion indicator is released, when corrosion starts, and changes color to indicate the presence of corrosion. In the same manner, the microcapsule can release corrosion inhibitors on demand when needed and where they are needed. This is advantageous because the encapsulated inhibitors, when incorporated into a coating, will be protected and prevented from interacting with other coating components.

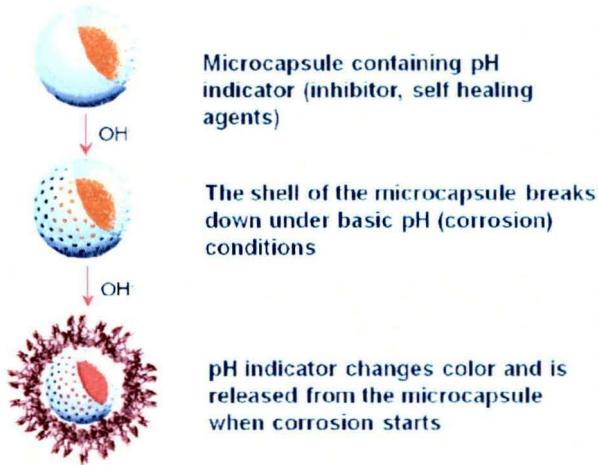


Figure 3: pH sensitive microcapsule concept

Smart Coating Based on pH Sensitive Microcapsules

Microencapsulation is a versatile approach because it can be used to encapsulate an unlimited number of materials, in both solid and liquid phase, and even in the gas phase when entrapped in a material such as aerogel. It is possible to incorporate microcapsules into composites or coatings. For corrosion applications, various compounds, such as corrosion indicators, inhibitors, self-healing agents, and dyes can be encapsulated. These microcapsules can be incorporated into various coating systems for corrosion detection, protection and self-repair of mechanical coating damage (Figure 4). The versatility of the design is of special interest in corrosion inhibition applications. Almost all corrosion inhibitors are chemically active reagents. Very often, the reactivity that makes them effective corrosion inhibitors also causes them to be environmentally unfriendly, such as in the case of chromates. Because of this, research for new and environmentally friendly corrosion inhibitors is an on-going effort in the corrosion protection industry. After a new inhibitor is developed, it usually takes a long time to incorporate it into a paint formulation. Microencapsulation of the inhibitor can shorten this long reformulation process because it prevents the interference of the inhibitor with other paint components. The pH-controlled release microcapsule design has, in addition to all the advantages of the microcapsule design, the true controlled-release function for corrosion applications. Most microcapsule applications involve the release of the core contents when the microcapsules are mechanically broken. However, pH sensitive microcapsules are specifically designed to release their contents when corrosion occurs. Mechanical damage in a coating is one of the important causes for corrosion of the base metal. However, many forms of defects in coatings, such as air bubbles, uneven thickness, permeation, porosity or edge effects, will also result in poor corrosion protection of the coating and allow corrosion to occur. pH sensitive microcapsules will release their content for corrosion detection or protection regardless of the corrosion cause.

CHEMISTRY OF PH SENSITIVE MICROCAPSULES

The pH sensitivity of the microcapsules enabled by a base-catalyzed ester hydrolysis. The polymeric walls of the microcapsules include a cross-linking agent that has one or more ester and mercapto groups. A typical cross-linker is pentaerythritol tetrakis (3-mercaptopropionate) (PTT), a tetra-functional molecule whose structure is shown in Figure 5.

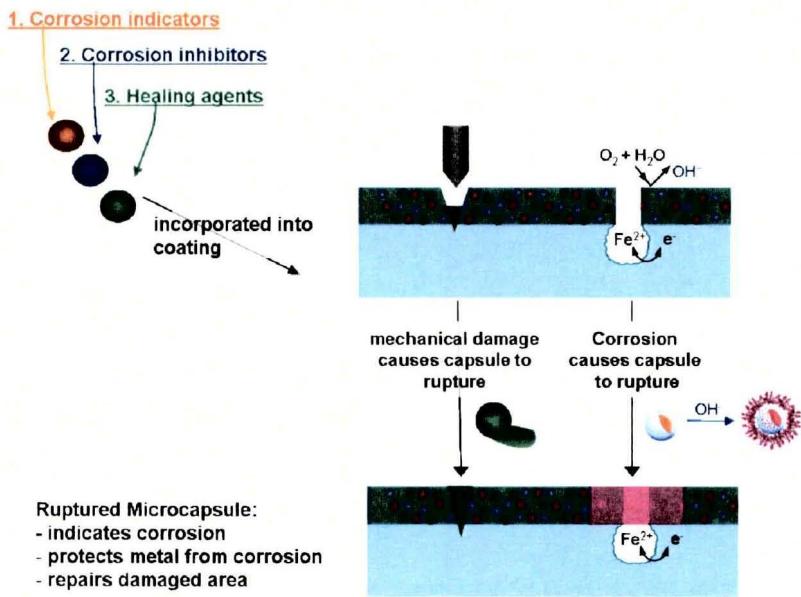


Figure 4: Conceptual illustration of a smart coating with pH sensitive microcapsules for corrosion detection and protection applications.

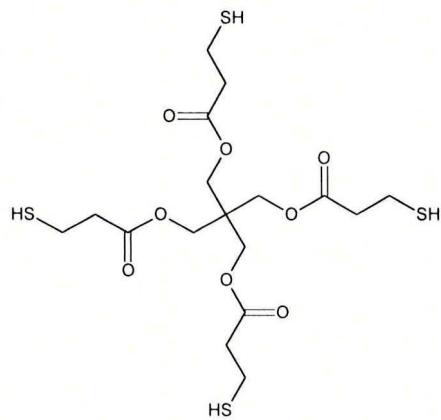


Figure 5: Structure of pentaerythritol tetrakis (3-mercaptopropionate) (PTT).

Since this cross-linker is not a good film former, other pre-polymers or monomers are needed to provide the structural integrity of the microcapsule wall. Examples of film-forming monomers and pre-polymers include urea formaldehyde and melamine formaldehyde monomers and pre-polymers. Capsule wall breakdown under basic conditions can be observed visually. Figure 6 shows such a breakdown as it occurs when microcapsules are exposed to a small amount of water containing sodium hydroxide, NaOH, (pH of 12). Soon after the microcapsules are exposed to the NaOH solution, the solution starts to penetrate the microcapsule wall, as indicated by the color change of the encapsulated pH indicator (Frames b-d). In frame e, the microcapsule begins to slowly release its contents (as evidenced by the small droplet that begins to form on the bottom left quadrant of the frame). The presence of droplets observed inside the microcapsules is due to the fact that the core content of the microcapsule is not miscible in water (oil-core microcapsule). The content continues to be released until

(as seen on frame i) it dissipates into the solution. The microcapsule wall eventually disintegrates as shown in frames j through n.

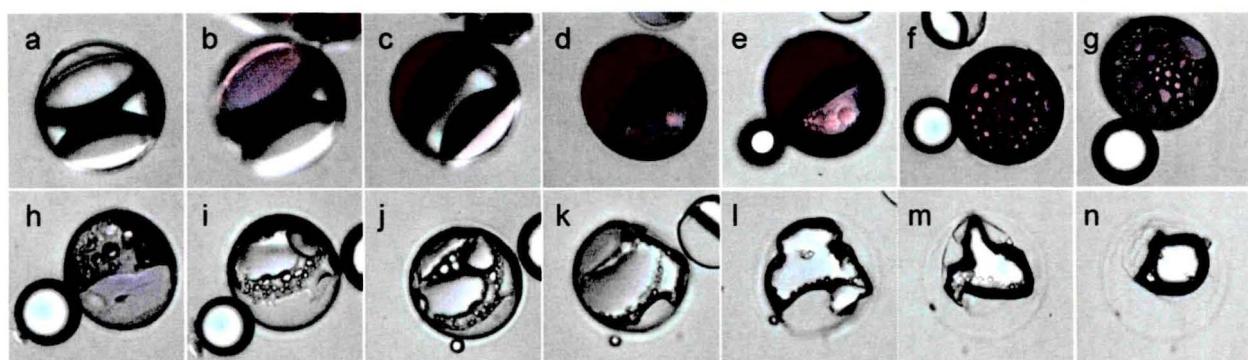


Figure 6: Microcapsule breakdown in basic solution.

EXPERIMENTAL PROCEDURE

Encapsulation Methods

Several methods such as spray drying, emulsion polymerization, interfacial polymerization, as well as *in-situ* polymerization have been used to synthesize pH sensitive microcapsules. Interfacial polymerization is illustrated in Figure 7 as an example. There are two main steps involved in the interfacial polymerization process: microemulsion formation and microcapsule wall formation. This technique can be used to form both oil (or hydrophobic) core and water (or hydrophilic) core microcapsules. Figure 7 shows a schematic representation of the steps involved in forming oil-core microcapsules: the microemulsion is formed by adding the oil phase (with pre-polymer, shown in yellow) to the water phase (with surfactant, shown in blue) and mixing. The last step is the formation of the microcapsule wall (shown in green) by interfacial polymerization. Figure 8 shows a schematic representation of the steps involved in forming water-core microcapsules: in this case, the microemulsion is formed by adding water (shown in blue) to the oil (with prepolymer and the surfactant, shown in yellow) followed by mixing; the last step is the formation of the microcapsule wall (shown in green) by interfacial polymerization.

The two illustrations below show the use of oil (hydrophobic solvent) soluble wall forming pre-polymer. A similar process can be developed to use water soluble wall forming materials by dissolving the wall forming pre-polymer in the water phase and the catalyst in the oil phase. The reaction at the interface will form the capsule.

In situ polymerization is also used to form pH sensitive microcapsules. The distinguishing characteristic between interfacial polymerization and *in situ* polymerization is that in the latter, polymerization occurs in the continuous phase and the polymer formed deposits at the interface to form the capsule shell. Spray drying involves dispersing the wall forming pre-polymer and component to be encapsulated (the core material) into a continuous phase (water for instance). The mixture is sprayed into a mist and in a hot gas flow where the liquid droplets are dried into solid particles. In the process, the core material is encapsulated inside the wall materials.

Interfacial and *in situ* polymerization are the main approaches used by the authors for microcapsule synthesis. Spray drying has been used to synthesize solid core microcapsules and as a useful method for drying microcapsules into a free flowing powder form without forming clusters.

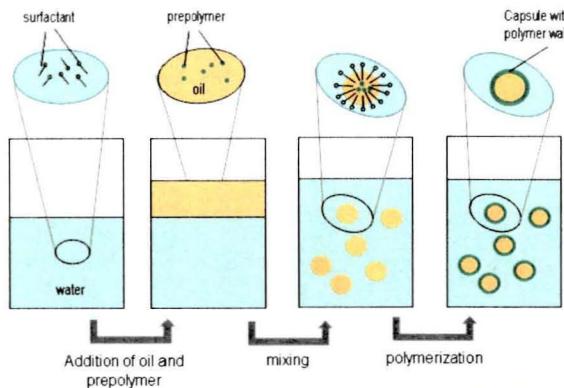


Figure 7: Schematic representation of the steps involved in the interfacial polymerization of an oil-in-water microemulsion for making oil-core microcapsules. Oil is shown in yellow and water in blue.

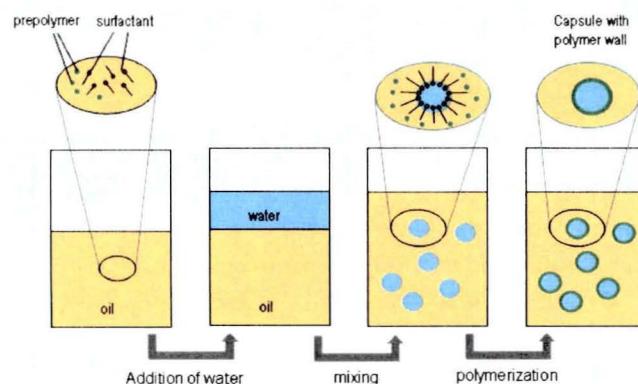


Figure 8: Schematic representation of the steps involved in the interfacial polymerization of a water-in-oil microemulsion to synthesize water-core microcapsules. Oil is shown in yellow and water in blue.

Microcapsule Synthesis

Different active core contents have been encapsulated, including corrosion indicators, corrosion inhibitors, dyes, and self healing agents using the methods described above. These procedures have been tailored for encapsulating corrosion inhibitors and indicators. Various indicators and inhibitors were selected and tested for their indicating and inhibiting efficiency respectively. The solubility and dispersibility of the active compounds were surveyed or tested to find a suitable method for their encapsulation.

In general, an active compound that can be dissolved or dispersed in a hydrophobic solvent, such as oil, can be encapsulated into oil-core microcapsules. Normally, oil core microcapsules are used for encapsulating oil soluble materials but not water soluble materials, such as salts or polar molecules. However, these materials can still be encapsulated by dissolving them first into a polar co-solvent and adding the resultant solution to the oil phase. Alternatively, a surfactant can be added to the oil phase. This will dissolve or disperse the polar or water soluble reagents into the oil phase. The oil-in-water

emulsion can then be formed and the interfacial reaction can be used to encapsulate these reagents into the oil core of the microcapsules.

Similarly, if a compound can be dissolved or dispersed in water, with or without the aid of a co-solvent, or a surfactant, it is possible to encapsulate it into water-core microcapsules. For example, phenolphthalein does not dissolve in water, but ethanol can be used as a co-solvent to dissolve a moderate amount of the indicator in water, making it possible to encapsulate it into water-core microcapsules (Figure 9).

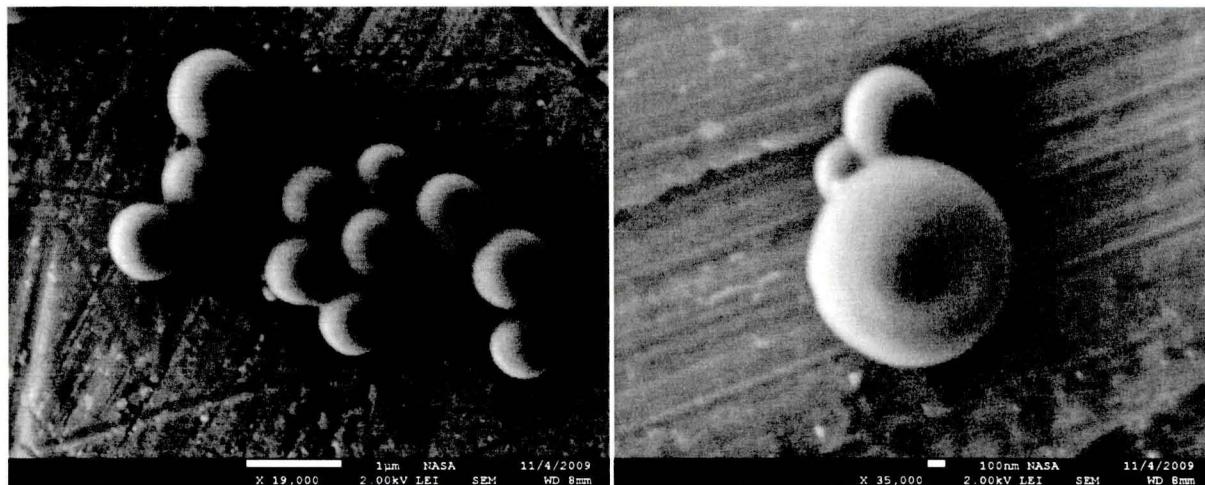


Figure 9: SEM images of the water-core microcapsules with phenolphthalein

Various compounds of interest for corrosion control applications have been encapsulated into oil-core microcapsules. These compounds include: corrosion indicators such as phenolphthalein, phenol red, and fluorescein; dyes such as Rhodamine B; healing agents such as epoxy and polysiloxane (Figure 10); and various solvents, such as chlorobenzene, which can be used as a healing agent.

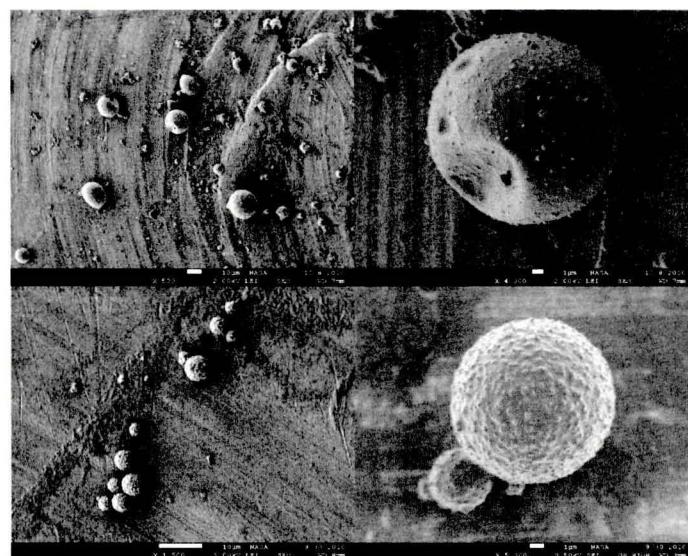


Figure 10: SEM images of microcapsules containing siloxane healing agents. Microcapsules synthesized by interfacial polymerization (top) and by *in situ* polymerization (bottom).

Various corrosion inhibitors and indicators have been encapsulated into water-core microcapsules, such as the corrosion indicator phenolphthalein, and corrosion inhibitors sodium molybdate (Na_2MoO_4), cerium nitrate ($\text{Ce}(\text{NO}_3)_3$), sodium phosphate (NaH_2PO_4), calcium metaborate, and phenylphosphonic acid.

After a microcapsule formula is developed, an optimization process usually follows to obtain microcapsules of suitable size and desired properties for its application. The capsule size can be controlled by adjusting the emulsion formula or by varying the mixing speed of the mixer during the emulsion formation. These methods can be used to obtain microcapsules of a desired size within a narrow range of distribution. Sizes from 200 nm to 200 μm (micron) can be obtained, with a typical size from about 1 to 5 μm . Oil-core microcapsules of various sizes are shown in Figure 11.

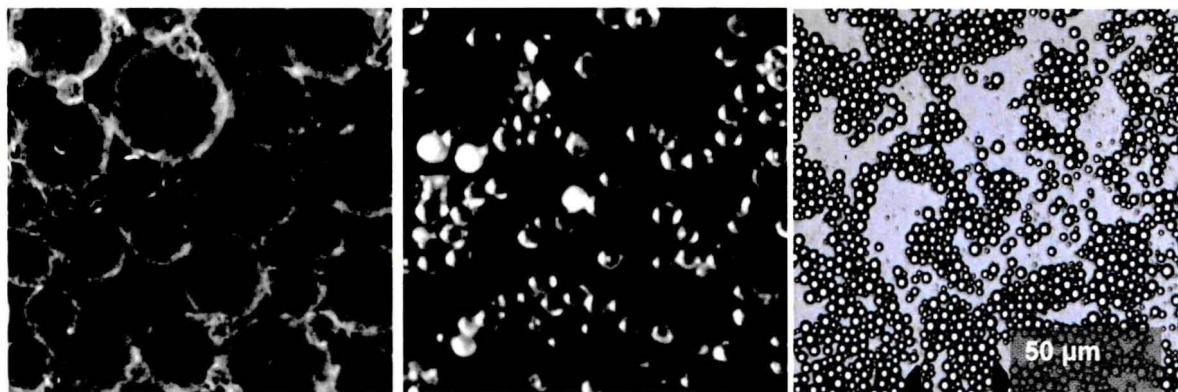


Figure 11: Oil-core microcapsules of different sizes.

The SEM images in Figure 12 show capsules of spherical shape with less than 1 μm in diameter size. The capsule wall thickness is about 50-100 nm as shown in the SEM images of the microcapsules obtained using a transmission electron detector (Figure 13).

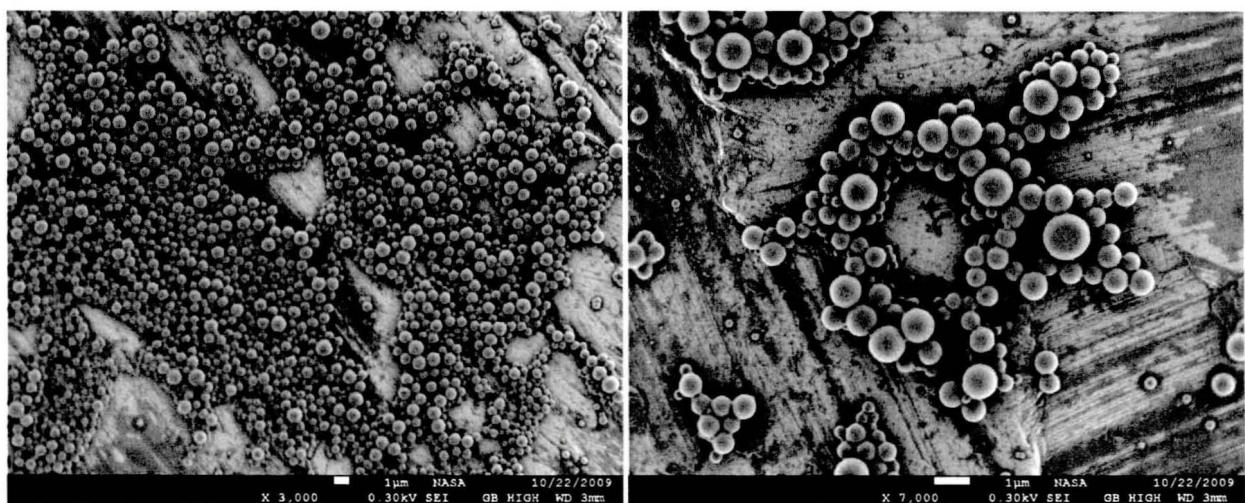


Figure 12: SEM Images of the water-core microcapsule.

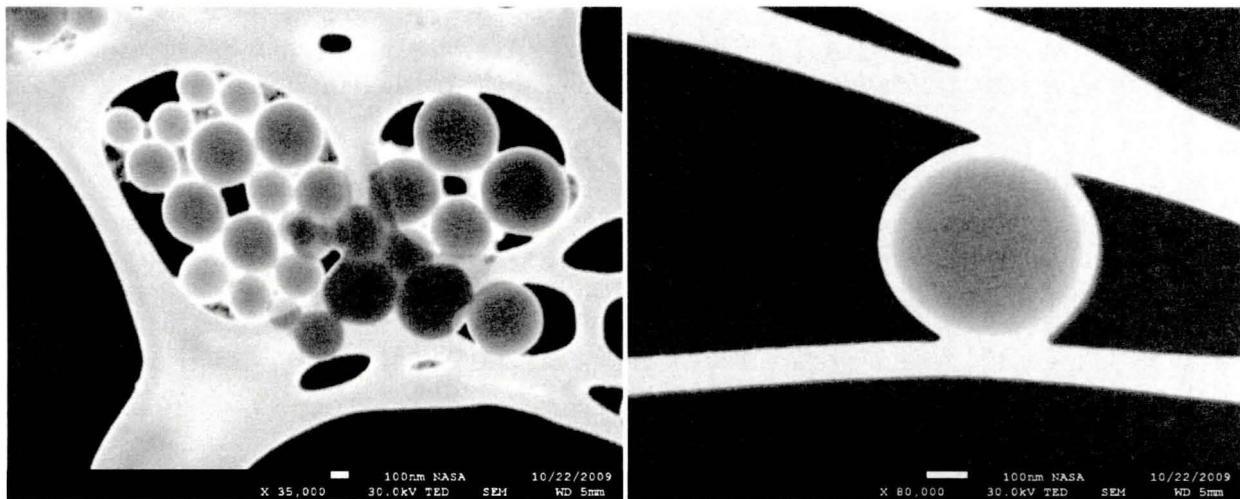


Figure 13: SEM images of a water-core microcapsule obtained by using a transmission electron detector.

Self-healing agents were selected for encapsulation by *in-situ* polymerization and interfacial polymerization methods using melamine formaldehyde pre-polymers as microcapsule wall forming materials. PTT was used to improve the mechanical strength, as well as, the solvent resistance of the microcapsule walls. The encapsulated systems were designed to rupture when a coating is damaged and deliver the healing film forming compound(s) to repair the damaged area. Six candidate self-healing systems were selected for encapsulation. Three of the candidate systems involved encapsulation of each separate component in a two part self-healing system and incorporation into a 2-part epoxy coating for testing. These systems included: two part epoxy (resin and hardener), two part siloxane (siloxane resin and catalyst), and a two part acrylate (acrylate monomer and UV activator). The other candidate self-healing systems can be described as solvent-born systems. These systems included: encapsulated solvent, encapsulated solid epoxy powder coating resin (dissolved in methyl benzoate), and encapsulated bisphenol A dianhydride (BPADA) monomer (dissolved in methyl benzoate).

Encapsulated corrosion indicators, inhibitors, and self-healing systems were incorporated into different commercially available coatings in order to test their corrosion indication, inhibition, and self-healing functions. Preliminary results of these tests are presented below.

RESULTS

Corrosion Indication Tests Results

Corrosion indication is one of the functions of the smart coating for corrosion detection, control, and self healing. This function can be incorporated into the coating by encapsulating a corrosion indicator into pH sensitive microcapsules. Figure 14 shows salt immersion test results from steel panels coated with a clear urethane coating containing 10% of microcapsules with corrosion indicator. The panels were scribed, immersed in 3.5% sodium chloride (NaCl) solution, and observed for visual changes over time. It was observed that the indicator signaled the onset of corrosion in the scribe about 1 minute after immersion, which is considerably earlier than the 2 hours it took for the appearance of the typical color of rust.

In addition to early corrosion detection, another potential application of the smart coating is to detect hidden corrosion. Bolts tend to corrode on the hidden shaft area before visible corrosion is seen on the

bolt head or nut. Often, the head and nut are in pristine condition, even when significant corrosion has occurred on the shaft (Figure 15). There is no method to identify the degree of corrosion without removing the bolt from service. A coating that changes color on the bolt head or nut, when corrosion starts, would greatly facilitate the corrosion inspection process. A conceptual illustration of how these coatings can be used to detect hidden corrosion on structural bolts is shown in Figure 16.

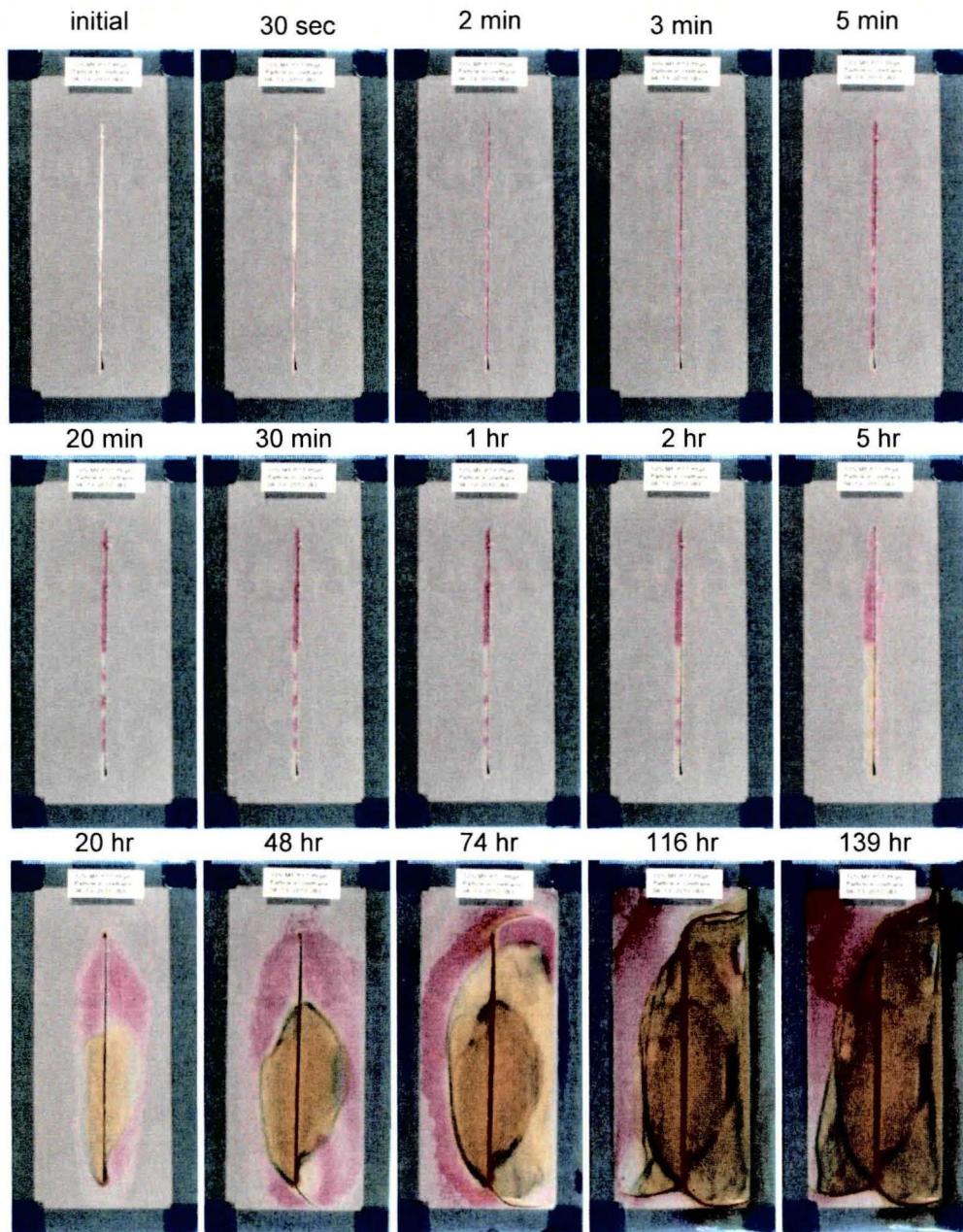


Figure 14: Corrosion indication test results.

An experiment was designed to test the ability of encapsulated phenolphthalein to detect hidden corrosion when incorporated into a coating system. Several coating systems (Table 1) were prepared in order to find a coating system that would indicate crevice corrosion as can be expected to occur in the nut and bolt set up. As can be seen in Figure 17, the epoxy/urethane coating system showed the ability of the coating to indicate hidden corrosion as evidenced by the appearance of the purple color.



Figure 15: Hidden corrosion of bolt

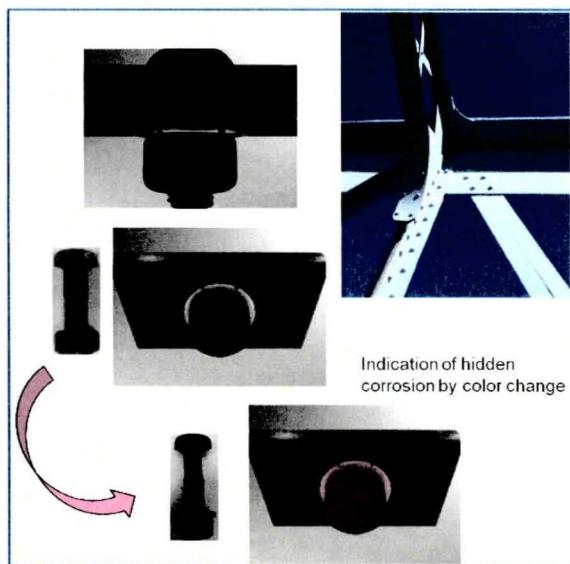


Figure 16: Conceptual illustration of hidden corrosion indication in structural bolts.

Corrosion Inhibition Tests Results

Test panels coated with CarboLine Carbomastic 15 FC epoxy mastic containing water-core microcapsules with an inhibitor have been tested using a salt fog chamber, for approximately 6 months, following the ASTM B117 standard method.⁹ Panels were evaluated for both rust grades (ASTM D610)¹⁰ and scribe ratings (ASTM D1654).¹¹ Several coating systems were tested; the coating containing 10% phenylphosphonic acid microcapsule performed the best. The corrosion ratings of these panels and are shown in Table 2, in comparison with the controls.

The pictures on Figure 18 show the test panels after 6 month of salt fog testing. While the control shows blisters and corrosion under paint, the phenylphosphonic acid (PA) microcapsule containing panel shows no sign of corrosion. In order to evaluate the scribe areas, the coating around these areas on the panels were scraped off for easy observation (shown in figure 19. It was found that the PA microcapsule containing coating showed much better adhesion than the control.

Table 1. Coating systems used for hidden corrosion indication testing.

System number	Metal Substrate	Coating systems
1	Zinc galvanized nut and bolt	Clear urethane coating containing 10% phenolphthalein (phph) microcapsules.
2	Zinc galvanized nut and bolt	First coated with epoxy, then top coated with clear urethane containing 10% phph microcapsules.
3	Sand blasted nut and bolt.	The ends of the nut and bolt were coated with inorganic zinc coating; the entire nut and bolt was coated with urethane containing 10% phph microcapsules.
4	Sand blasted nut and bolt	The ends of the nut and bolt were coated with inorganic zinc coating. The entire nut and bolt was coated with epoxy and then top coated with a clear urethane containing 10% phph microcapsules.



5	Zinc galvanized nut and bolt	The ends of the nut and bolt were coated with urethane containing 10% phph microcapsules.
6	Zinc galvanized nut and bolt.	The ends of the nut and bolt were coated with epoxy and then top coated with urethane containing 10% phph microcapsules.

Figure 17: Indication of hidden corrosion after 600 hours of salt fog exposure.

Table 2: Rust Grade and Scribe Rating of Carbomastic 15 FC experimental coatings

Carbomastic 15 FC Coating Systems	Sample #	Rust Grade	Scribe Rating
Control	1	5	5
	2	10	5
	3	6	5
10% (w/v) phenylphosphonic acid microcapsule	1	10	5
	2	10	5
	3	10	5

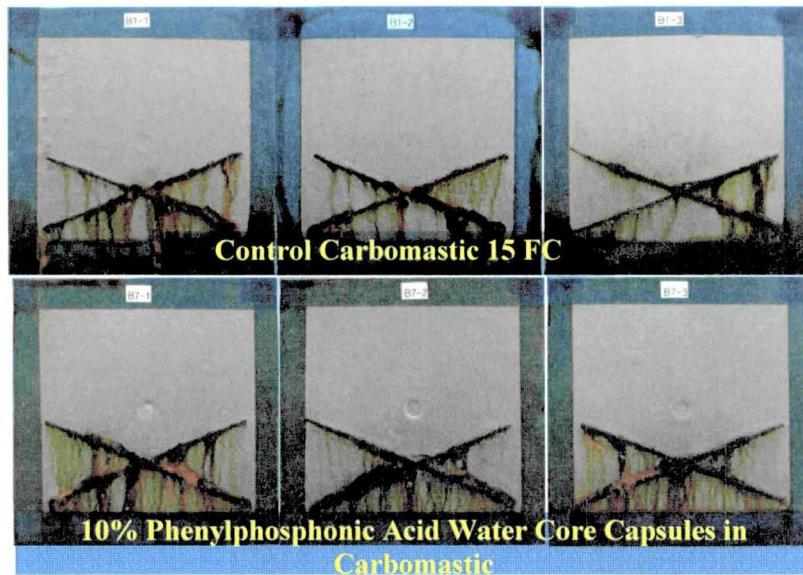


Figure 18. 6 month Salt fog test results of selected coating systems.

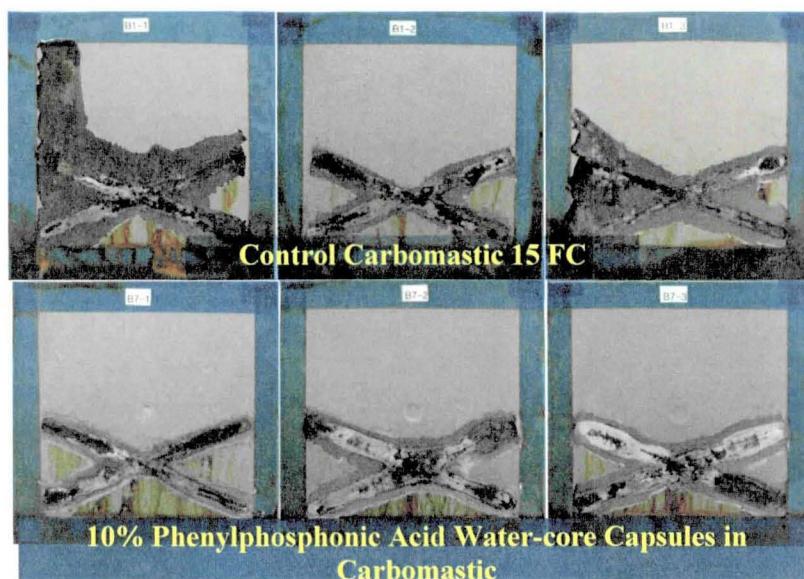


Figure 19: 6 month Salt fog test results of selected coating systems.

Self-healing Tests Results

Test coatings were prepared by incorporating the self-healing system of interest into a 2-part epoxy coating and applying it to steel panels. The thickness of the applied coatings was approximately 250 to 400 μ p. The steel panels were tested using the ASTM B117 salt fog test procedure. In order to evaluate the healing performance of each self healing system, three parallel scribes of different widths were made on each coated panel. The best healing performance was observed in the two capsule siloxane healing system. Some siloxane systems exhibited excellent corrosion protection when compared to control (as shown in Figure 20).

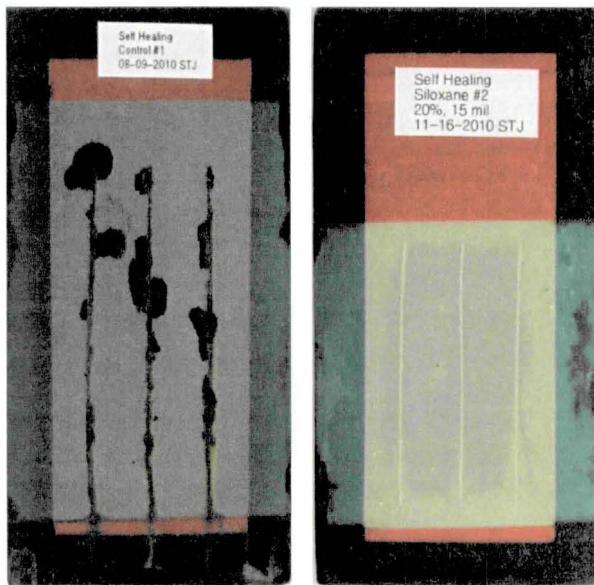


Figure 20: 700 hours of salt fog testing results of carbon steel panels coated with a control coating system (left panel) and the same coating with a siloxane healing system (right panel).

CONCLUSIONS

A multifunctional smart coating for the autonomous control of corrosion is being developed using pH-sensitive microcapsules. The microcapsules are designed specifically to detect the pH changes that are associated with the onset of corrosion and respond autonomously to indicate its presence early, to control it by delivering corrosion inhibitors, and to deliver self healing or film forming agents capable of repairing mechanical damage to the coating.

Various pH-sensitive microcapsules with hydrophobic or hydrophilic cores were synthesized through interfacial polymerization reactions in an emulsion. The microencapsulation process was optimized to obtain monodispersed microcapsules in a size range suitable for incorporation into commercially available coatings. The microcapsules can be harvested in suspension or in free-flowing powder form. Preliminary results from salt fog testing of panels coated with commercially available coatings, in which the microcapsules were incorporated, indicate that microcapsules can be used to detect corrosion before visible rust appears and to deliver corrosion inhibitors.

Current work is being focused on optimizing the concentration of indicator in the microcapsules as well as on optimizing the release properties of the microcapsules when incorporated into coatings of interest. Candidate self healing systems have been encapsulated and tested for self-healing performance. Salt fog test results revealed that the 2-capsule siloxane resin system had the best self-

healing performance. Methods designed to accomplish good self-healing corrosion control in thinner films are being evaluated.

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REFERENCES

1. L.M. Calle and Wenyan Li, "Coatings and Methods for Corrosion Detection and/or Reduction" U.S. Patent No. 7,790,225, U.S. Patent and Trademark Office, 2010.
2. F. J. Maile, T. Schauer, and C. D. Eisenbach, "Evaluation of Corrosion and Protection of Coated Metals with Local Ion Concentration Technique (LICT), *Progress in Organic Coatings*, Volume 38, (2000): page 111.
3. W. Li and L. M. Calle, "pH and Electrochemical Responsive Materials for Corrosion Control Applications," CORROSION/08, paper no. 08214, (Houston, TX: NACE, 2008).
4. M. R. Kessler, "Self-healing: a New Paradigm in Material Design," Proceedings of the Institution of Mechanical Engineers (IMechE), Part G: J. Aerospace Engineering, Volume 221, (2007): pages 479-495.
5. M. Anderson, G. O. Wilson, and S. R. White, "Evaluation of Self-Healing Polymer Chemistries for Application in Anti-Corrosion Coatings," American Coatings Conference, June 2-4, 2008.
6. S. H. Cho, PhD Thesis "Polydimethylsiloxane-Based Self-healing Composite and Coating Materials", University of Illinois at Urbana-Champaign, Urbana IL, 2006.
7. W. Li and L. M. Calle, "Controlled Release Microcapsules for Smart Coatings," CORROSION/07, Paper no. 07228, (Houston, TX: NACE, 2007).
8. W. Li and L. M. Calle, "A Smart Coating for the Early Detection and Inhibition of Corrosion," Proceeding of the Smart Coatings 2007 Conference, February 2007, p.191.
9. ASTM⁽¹⁾ B 117-09, "Standard Practice for Operating Salt Spray (Fog) Apparatus," (West Conshohocken, PA: ASTM).
10. ASTM D610-08, "Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces,"
11. ASTM D1654-08, "Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments," (West Conshohocken, PA: ASTM).

⁽¹⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.